Removal and Recovery of Levafix Brilliant Red E-4BA and Levafix Brilliant Red E-6BA from Aqueous Solution by MembraneTechnique

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Abstract- **The transport and recovery of Levafix brilliant red E-4BA and Levafix brilliant red E-6BA were investigated using polypropylene (PP) and polytetrafluoroethylene (PTFE) fiber based supported liquid membrane containing tetra butyl ammonium bromide (TBAB) in coconut oil as a carrier. The influencing parameters studies are: pH of the feed solution, concentration of dye in the feed solution, extractant concentration, various kind of stripping agent, rate of stirring, time of transport, reusability of membrane and stability of membrane. Increase in TBAB concentration inside the membrane enhances the flux with its maximum value at 1.553×10^{-4} M TBAB. Further increase in the concentration of TBAB leads to decreased rate of transport due to increase in viscosity of membrane liquid. The optimum conditions for dye transport are: pH of feed (7 ± 0.1), 1.553×10^{-4} M extractant concentration, 350 rpm for stirring, 4.9×10^{-1} M potassium hydrogen phthalate as a stripping solution, the time of transport 6 h. It was noticed that flux values were increased with increasing dyed concentration in the feed phase. Applying this study to textile wastewater, dyes were transported up to 98% in 6h. This recovery technique is rewarding to environment and economy.**

Keywords- Transport; Polytetrafluoroethylene; Extractant; Reusability; Viscosity

I. INTRODUCTION

Textile industries use dyes or pigments to colour their final products. Dyes have a synthetic origin and complex aromatic molecular structures. They are inert and difficult to biodegrade when discharged into waste streams. This aspect has always been overlooked in their discharge[1]. Discharging dyes into the hydrosphere can cause environmental damage and it gives undesirable colour[2, 3]. Approximately 10-15% of the azo dyes are released into the environment mainly via wastewater[4]. This is very dangerous because some of the azo dyes and their degradation products have a toxic, mutagenic or carcinogenic influence on living organisms. Therefore, the azo dyes containing wastewater should be treated before their discharge[5]. Dyes are classified according to their structure as anionic and cationic[6]. In aqueous solution, anionic dyes carry a net negative charge due to presence of sulphate groups, while cationic dyes carry a net positive charge due to presence of protonated amine or sulphur containing groups[7]. So far, many methods, such as flocculation and coagulation[8-12], the chemical oxidation including fenton's reagent[13-18], ClO_2, NaClO or O_3[19], etc., air flotation processes adsorption by resins or activated carbon, activated sludge, anaerobic-aerobic two stage biochemical process[20-22], electrolytic[23, 24] and high impulse current[25] have been used to treat the wastewater.

The above mentioned methods are only removing the colours and not recovering the dyes from wastewater. Liquid-liquid extraction (LLE) is significant potential to remove the dyes from wastewater[26]. However, the few research works have been reported about recovery of the dyes from wastewater. Hushenghu et al.[27] reported that the strong acid dyes are recovered from wastewater by solvent extraction method. This method not only recovers the dyes from wastewater but also can make the effluent quality meet first order criterion of national discharge standards. Muthuraman and Palanivelu[28] also reported the recovery of the dyes from aqueous solution using Tri-n-butyl phosphate as a carrier by LLE method. It was recently reported[29] that the acid orange II dye wastewater could be treated by solvent extraction method to recover the dyes from effluent. LLE is a traditional technique for extraction of organic analytes from aqueous solution. The technique is well-known and still widely used, although now it is less attractive comparing to supported liquid membrane (SLM). This is because LLE (i) is tedious and time consuming (ii) is not easy to automate (iii) it forms emulsions (iv) it is environmentally unfriendly due to large volume of organic solvents used[30].

Supported liquid membrane is a good alternative technique to recover the organic compounds and metal ions from wastewater. In SLM, the separation of chemical species using a thin layer of organic solution absorbed in the pores of polymeric support. This membrane acts as an intermediate in separating the feed phase, which containing the species to be removed, and the strip phase in which the species to be transferred is recovered. As in solvent extraction, the extractant is responsible for extraction of the species interest; in this case, however, the extraction and recovery processes are carried out simultaneously, with the advantage that, unlike solvent extraction, SLM uses minimum quantities of organic phase[31], which allows the use of highly selective extractants and diminishes the risk of environmental contamination at the same time. Recoveries of organic compound by supported liquid membrane have been reported. Transport of sodium phenolate through SLM was studied by Sanwook Park et al.[32]. In this study, tricaprylmethyl ammonium chloride or dibenzo 18 crown 6 (DBC) was used as a carrier. Monosaccharide was recovered from aqueous solution by SLM containing the resorcinarene carrier. The rate determining step in the transport mechanism was shown to be the migration of 1:1 carrier–sugar complex in the immobilized organic phase[33]. Effluent from FCC (fludized bed catalytic cracking) process containing phenol was recovered. The permeation rate increased with pH and reached a plateau at pH above 13[34]. Jason Clark et al.,[35] reported the recovery of amino acid from racemic mixture of phenylamine and methionine. The extraction of peptides through a supported liquid membrane containing di-2-(ethylhexyl) phosphoric acid (D2EHPA) as a carrier was studied by Drapah and Wieczorek[36]. Muthuraman and Palanivelu[37] also reported

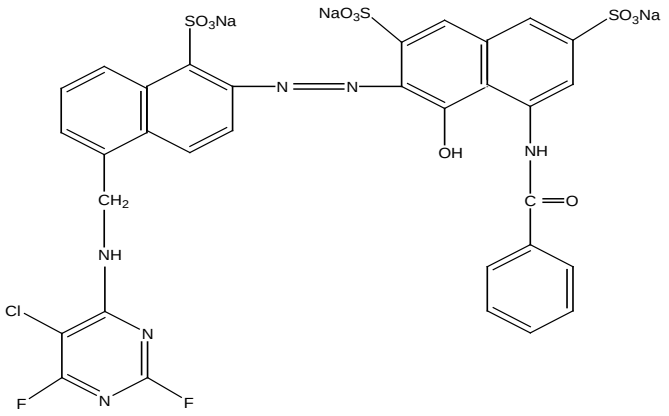
that removal and recovery of textile dye from aqueous solution using renewable, nontoxic, natural vegetable oil have been used as liquid membrane. Apart from organic compounds, some of the toxic metals such as Cr, Ni, Cu, Zn, and Mo (VI)[38-41] have been recovered from wastewater by supported liquid membrane.

In this paper, the recovery of dyes namely Levafix brilliant red-E4BA a Levafix brilliant red-E6BA is henceforth called as LBR-E4BA, LBR-E6BA. The following parameters such as pH variation in the feed solution, various types of stripping agents, rate of stirring, time of transport, stability of membrane, Tetra butyl ammonium bromide (TBAB) concentration in the membrane phase and reusability of membrane have been studied. The mechanism of dye transport for TBAB base SLM has also been explained.

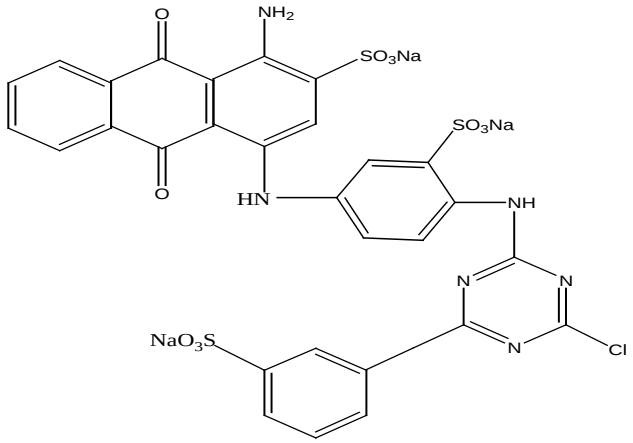
II. EXPERIMENTAL METHODS

A. Chemicals and Reagents

All the chemicals used were of analytical grade reagents. They were used as supplied TBAB (>99.8%), potassium hydrogen phthalate (>99.5%), sulphuric acid (98.0%), sodium hydroxide (>96.0%) by Merck, Malaysia, coconut oil (local market). Anionic dyes (LBR-E4BA, LBR-E6BA) were supplied by DyStar, Mumbaii. The structures of dyes and carriers were given in Fig. 1. And Fig. 2 Polytetra fluoroethylene (PTFE) supported membrane 1 µm pore size and 10 µm thickness having 75% porosity was obtained from PALL pharma lab (India).



a. Levafix brilliant red E4BA



b. Levafix brilliant red E6BA

Fig. 1 Structure of dyes

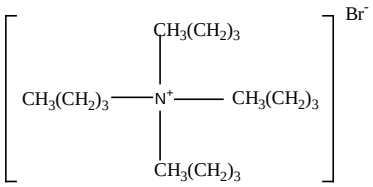


Fig. 2 Structure of Tetra butyl ammonium bromide

B. Instruments

A Spekol 1200, UV spectrophotometer was used to measure the dye concentration in the initial and final feed solution. To mix feed and strip solution, stirrer was used. During the supported liquid membrane study, pH of the feed solution was constantly measured at a time interval of 10 minutes by pH meter (WTW, Germany). Conductivity meter and total organic analyzer (Analytical Jena, Germany) were also used to measure conductivity and organic contain of solution. Electrophoresis (Analytical Jena, Germany) was used to find out nature of dyes.

C. Membranes

The support for the organic liquid phase PTFE film was used. It is a hydrophobic synthetic polymer having high porosity, low thickness and chemically stable. It has 75% porosity with 0.5 µm pore size. The supported liquid membrane has an organic phase that contains carrier, in the polymeric porous medium. In the transport study of dyes, TBAB was selected as an organic carrier and coconut oil as a diluent. The coconut oil containing carrier was incorporated into the support membrane by capillary action forming a liquid membrane. The membrane was soaked in organic carrier solutions i.e. TBAB/coconut oil for 24 hrs.

D. Membrane Cell (Permeator)

The experiments were performed at 25 ± 1^0C with a simple batch type permeator (cell) shown in Fig. 3. The permeator was made of Perspex material consisted of two compartments of volume capacity 100 cm^3 with flanges to clamp the membrane between the compartments. The effective membrane containing area was 12.56 cm^2. Both the compartments had electrical stirrers to agitate the liquid at a speed greater than 300 rpm[42].

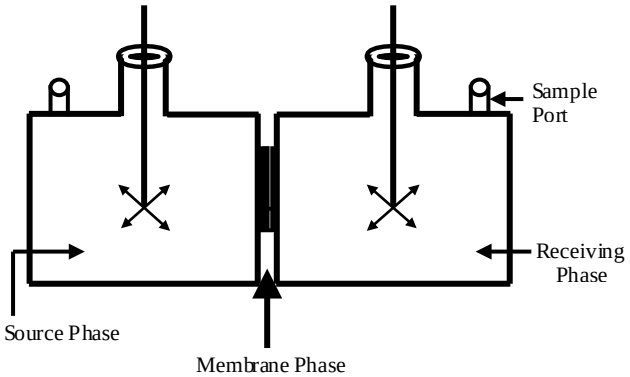


Fig. 3 Schematic diagram of supported liquid membrane reactor

E. Determination of Flux, Permeation Coefficient and Removal Efficiency

The dye flux[36] was obtained by following relation:

$$J = \frac{-VdC}{Adt} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where, V is the volume of feed solution, A is the membrane area in contact with aqueous solution and C is the concentration of dye.

The permeation coefficient (P) was calculated by the following equation[42].

$$\ln \frac{C_t}{C_0} = \frac{A}{V} P_t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where Co is the initial dye concentration in the feed solution, C_t is the feed concentration at the operating time of t, V is volume of feed solution, A is the membrane area in contact with aqueous solution, t is operating time (S).

The removal efficiency[38] was calculated as follows:

$$\text{Removal } (\%) = 100 \times (C_{F0} - C_{Ft}) / C_{Fo} \quad \ldots\ldots\ldots\ldots \quad (3)$$

F. Methods

The aqueous feed solution was adjusted to the desired pH value using dilute sulphuric acid or sodium hydroxide before starting of the experiments. 10% potassium hydrogen phthalate (KHP) solution was used as a strip solution in all experiments. The feed and strip solution were kept under agitation using electrical stirrers. Sampling was done by withdrawing 3.0 cm^3 of solution from both the reactor at preset time interval and the dye concentration was measured on UV spectrophotometer. The absorbance measured at 519 nm and 523 nm for LBR-E4BA and LBR-E6BA. The calibration was made in the concentration of range 0 to 50 mgL^{-1}.

G. Electrophoresis Study

A known concentration of dye solution was filled into the electrophoresis chamber (Kalpamac 250, Malaysia) and constant current at 50 V was run for 2 h. At the end of the second hour the sample was taken from anionic and cationic compartments and absorbance was measured. Qualitative decision was made as to whether dye was anionic or cationic[43].

III. RESULTS AND DISCUSSION

Liquid-liquid extraction was carried out before starting the supported liquid membrane study. A known volume (15mL) of dye solution (50mgL^{-1}) was taken into separating funnel and 15mL of TBAB-CH_2Cl_2 solution was added to separating funnel. The separating funnel is equilibrated with 10 min and both the layers were allowed to settle. Once the phases clearly separated, the aqueous layer was taken for measurement. In the organic layer, 15mL of stripping agent (10% KHP) was added and equilibrated again for 10mts and the layers were allowed to settle. Again after phase separation aqueous layer (stripped solution) was taken for measurement. In SLM study, coconut oil has been used as diluent instead of CH_2Cl_2. Since CH_2Cl_2 is toxic and stability of membrane was very less.

A. Effect of pH in the Source Phase

To study the effect of pH on recovery of dyes from aqueous solution of dye concentration in 50 mgL^{-1} pH of the feed solution was varied from 4.1 to 10.2. The extractant concentration in the membrane phase and KHP concentration in the strip phase were kept constant at 1.553 × 10^{-4} M and 10 % respectively. The flux values obtained at different pH were plotted in Fig. 4. It was observed from Fig. 4 the flux values are increased from pH 4 to 7 and decreased above 7. When the pH is increasing in the feed solution, dye molecules might be changed from its original structure that is why the transport rate of dyes decreased and flux also decreased. The optimum condition of pH is 7 ± 0.1 at 27^0C.

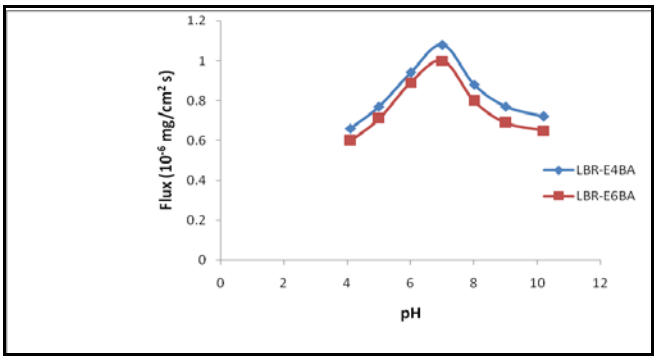


Fig. 4 Effect of pH in source phase (Experimental conditions: source phase 60mL of 50 mgL^{-1} dye at various pH, receiving phase 60 mL of 1.5 N of H_2SO_4 solution, stirring speed 350 rpm, carrier concentration 1.553 × 10^{-4} time of transport 6 h)

B. Effect of Carrier Concentration

The effect of TBAB concentration in the membrane phase was studied in the range of 3.88 × 10^{-5} M to 6.211 × 10^{-4} M. The pH of the feed solution was kept constant at 7.0 ± 0.2. The fluxes were calculated at different TBAB concentration and are shown in Fig. 5. It was observed that the flux increased from 8.4 × 10^{-6} mg/cm^2.s to 1.08 × 10^{-5} mg/cm^2.s for LBR-E4BA and 8.0 × 10^{-6} mg/cm^2.s to 1.05 × 10^{-6} mg/cm^2.s for LBR-E6BA. With the increase in TBAB concentration up to 1.553 × 10^{-4} M, further increase of carrier concentration flux decreases to 7.9 × 10^{-6} mg/cm^2.s for LBR-E4BA and 7.1 × 10^{-6} mg/cm^2.s for LBR-E6BA. The decrease of flux with increase of carrier concentration in membrane phase might be due to increase in viscosity of membrane phase, so the optimum concentration of TBAB is 1.533 × 10^{-4} M.

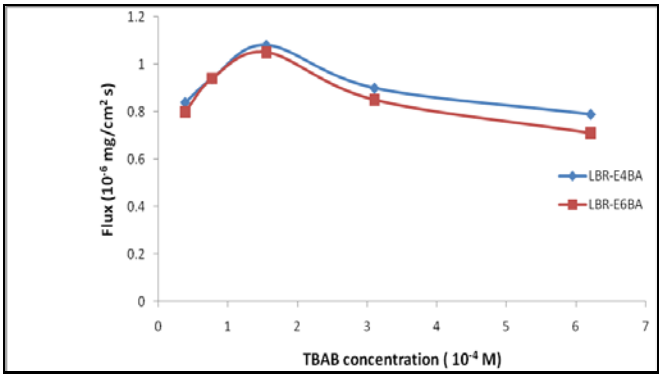


Fig. 5 Effect of carrier concentration (Experimental conditions: source phase 60mL of 50 mgL^{-1} dye at pH 7 ± 0.1 at 25^0C, receiving phase 60mL of 1.5 N of H_2SO_4 solution, stirring speed 350 rpm, carrier concentration different morality of TBAB, time of transport 6 h)

C. Influence of the Support Materials

Thickness and porosity of the support materials are fundamental parameter that acts on the stability of SLM. The influence of the parameters has been studied using PTFE membrane. The obtained results, reported in Table I. It shows flux values of the dye with different characteristics of support material. Flux values were increased with increase in the porosity of the support material and decreased with increase in the thickness of the support material.

TABLE I INFLUENCE OF THE SUPPORT MATERIALS

Types of Membrane	Thickness (μm)	Porosity (%)	Flux (10^5 mg/cm^2 s)	
			LBR-E4BA	LBR-E6BA
PTFE	90	76	1.08	1.06
PTFE	180	72	0.60	0.59

D. *Influence of the Dye Concentration*

Flux through the membrane interfaces depends on the initial dye concentration. Fig. 6 shows flux values were increased, increasing the initial dye concentration (50 to 500mgL^{-1}). However, beyond a concentration of 50mgL^{-1} the flux values were remained constant. This was due to the saturation of membrane at the strip interface and is most probably the limiting step.

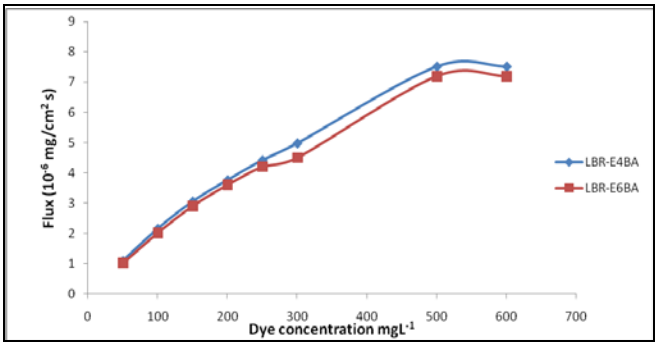


Fig. 6 Effect of initial dye concentration (Experimental conditions: source phase 60 mL of various concentration of dye at pH 7 ± 0.1 at 25^{0}C, receiving phase 60 mL of 1.5 N of H_2SO_4 solution, stirring speed 350 rpm, carrier concentration 1.553 × 10^{-4}, time of transport 6 h)

E. *Effect of Temperature*

Fig. 7 shows the variation of mass flux of dyes versus the temperature. The flux decreases drastically when increasing the temperature. This is probably due to the evaporation of the solvent in SLM at high temperature or to its release and solubility in aqueous phases when the temperature is increasing due to a viscosity decrease, causing the degradation of the SLM[44]. It can also be due to a lower complexation at higher temperatures. From Fig. 7 it is clear that the temperature was maintained at 25^{0}C.

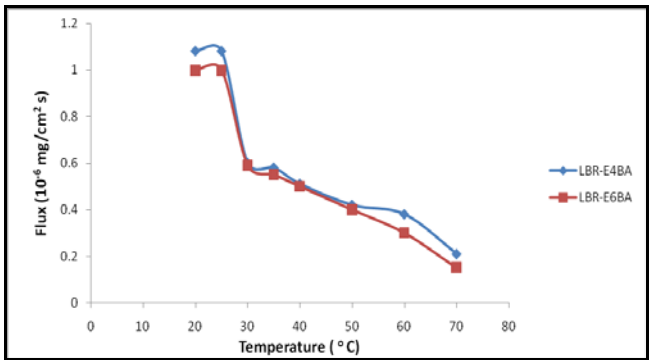


Fig. 7 Effect of temperature (Experimental conditions: source phase 60 mL of 50 mgL^{-1} dye at pH 7 ± 0.1 at different temperature, receiving phase 60 mL of 1.5 N of H_2SO_4 solution, stirring speed 350 rpm, carrier concentration 1.553 × 10^{-4}, time of transport 6 h)

F. *Effect of Stripping Phase Concentration*

The stripping reaction at the side of membrane-strip solution plays a vital role in the transfer of dye from feed side to strip side. If the dye in the dye-TBAB ion pair, to be completely stripped, the membrane phase was saturated with dyes and the permeation rate may therefore decrease stripping studies which were carried out in the range of 0.98 × 10^{-1} M to 4.90 × 10^{-1} M solution of KHP. From Table II the maximum stripping efficiency was found in the range of 4.90 × 10^{-4} M solution. Further increase in KHP concentration had no significant effect in stripping efficiency, and therefore, 4.90 × 10^{-1} M concentration of KHP was sufficient for stripping dye from membrane phase.

TABLE II STUDY OF STRIPPING AGENT CONCENTRATION

Stripping Agent conc.(10^{-1} M)	% of Dye Stripped		Absolute Amount mgL^{-1}	
	LBR-E4BA	LBR-E6BA	LBR-E4BA	LBR-E6BA
1.96	80.3	76.4	40.1	38.2
2.94	85.5	80.4	42.5	40.2
3.82	90.2	80.2	45.1	44.0
4.90	98.0	96.0	49.0	48.0

G. *Influence of Membrane Diluent on the Permeation of Dye*

The liquid membrane diluent is equally an important parameter to obtain a stable SLM as the characteristics of the diluents are mainly responsible for the stable liquid membrane phase. The results of dye permeation using various diluents are presented in Fig. 8. It can be seen that the best permeation was obtained when coconut oil and CH_2Cl_2 were used as diluent. In CH_2Cl_2 -TBAB system, the stability of membrane was very less comparing to coconut oil-TBAB. Further research is being carried out with coconut oil as a diluent.

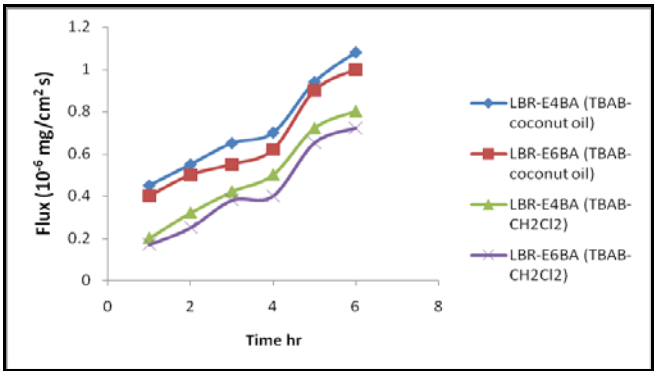


Fig. 8 Study of diluents on the permeation of dye (Experimental conditions: source phase 60 mL of 50 mgL^{-1} dye at pH 7 ± 0.1 at 25^{0}C, receiving phase 60 mL of 1.5 N of H_2SO_4 solution, stirring speed 350 rpm, carrier concentration 1.553 × 10^{-4}, diluent used coconut oil and methylene chloride time of transport 6 h)

H. *Influence of Stirring Speed*

In order to achieve effective permeation of dye in the SLM system, it is necessary to explore the effect of stirring speed on the transport flux. In the present investigation the stirring of the source and receiving phases were carried out from 50 to 450 rpm and the results were depicted in Fig. 9. The flux values are increased from 50 to 300 rpm and beyond that no appreciable increase was observed. Further a slight decrease in flux at 370 to 400 rpm could be due to the high turbulence caused by stirring, results in displacement of carrier from membrane pore[45]. The optimum condition of stirring speed is 350 rpm.

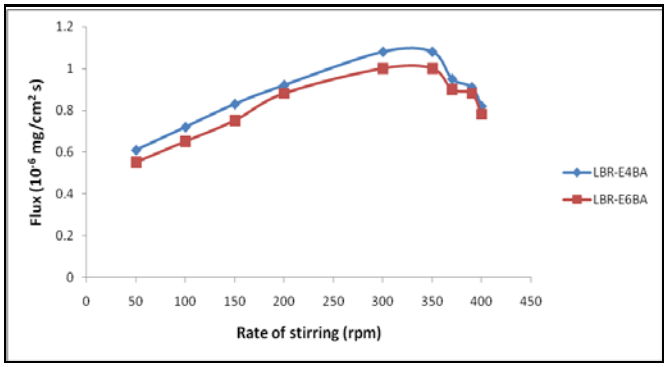


Fig. 9 Study of stirring speed (Experimental conditions: source phase 60 mL of 50 mgL^{-1} dye at pH 7 ± 0.1 at 25^{0}C, receiving phase 60 mL of 1.5 N of H_2SO_4 solution, carrier concentration 1.553×10^{-4}, time of transport 6 h)

I. *Transport Kinetics of Dyes*

The concentration time profile of dyes transport was studied over a period of 6h. Fig. 10 shows the time dependence of dye transport through the SLM containing TBAB under optimized condition. It is evident that there was a rapid rise in the dye concentration in the receiving phase, as well as sharp decrease in dye concentration in the feed phase during the transport study. At 6 h, the initial dye concentration of 50 mgL^{-1} with permeability coefficient value 8.65×10^{-4} mg/cm^2.s and 6.62×10^{-4} mg/cm^2.s for LBR E4BA and LBR E6BA (Fig. 11). The overall transport process in the SLM was controlled by diffusion in the micro porous membrane. However, some authors[46] have reported that the aqueous boundary layer diffusion and membrane diffusion was simultaneously the controlling factors in SLM.

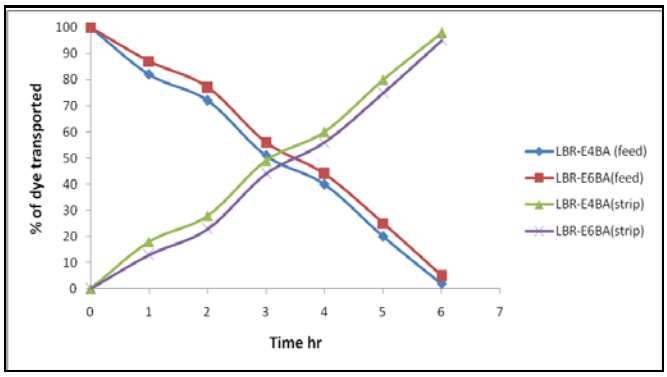


Fig. 10 Study of transport of dyes (Experimental conditions: source phase 60 mL of 50 mgL^{-1} dye at pH 7 ± 0.1 at 25^{0}C, receiving phase 60 mL of 1.5 N of H_2SO_4 solution, carrier concentration 1.553×10^{-4}, stirring speed 350 rpm)

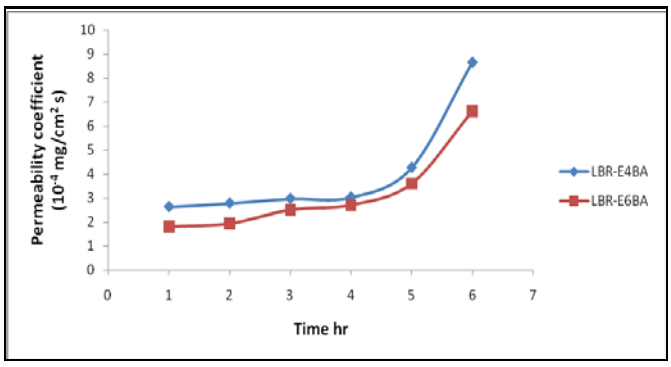


Fig. 11 Effect of permeability coefficient (Experimental conditions: source phase 60 mL of 50 mgL^{-1} dye at pH 7 ± 0.1 at 25^{0}C, receiving phase 60 mL of 1.5 N of H_2SO_4 solution, carrier concentration 1.553×10^{-4}, stirring speed 350 rpm, time of transport 6 h)

J. *Stability of Membrane*

One of the major problems concerning SLM is their low stability due to the loss of either a membrane solvent or an ion carrier. The characteristics of solvent and the corresponding solubility of the carrier seem to be the main reason, which cause this loss. Permeability coefficient has been used to evaluate the life time of SLM. The transport of dyes from aqueous solution at pH 7 ± 1 containing dye at the concentration of 50 MgL-1 through SLM with TBAB as an ion indicator into 4.9×10^{-1} M KHP aqueous solution was investigated. This experiment was repeated many times, where both aqueous and feed and receiving phase was renewed every time while the membrane remained the same as in the first run. Fig. 12 shows that, after 30 hr, the permeability decreases which might be due to either the membrane loss or accumulation of dye on the membrane. The factor such as surface shear forces changes with morphology, Margoni effect and Bernard effect also cause the membrane instability[47, 48]. One of the methods to enhance the SLM lifetime is the reimpregnation of the support with LM to keep the flux at constant level[49].

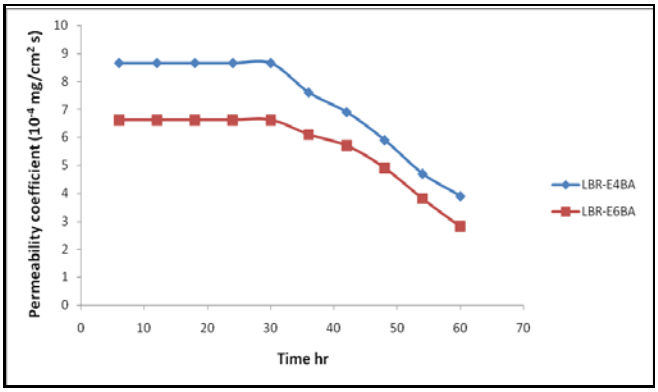


Fig. 12 Effect of stability of membrane (Experimental conditions: source phase 60 mL of 50 mgL^{-1} dye at pH 7 ± 0.1 at 25^{0}C, receiving phase 60 mL of 1.5 N of H_2SO_4 solution, carrier concentration 1.553×10^{-4}, stirring speed 350 rpm, time of transport 6 h)

K. *Reproducibility of SLM*

The reproducibility of the SLM technique was studied by performing five replicates transport experiments. The relative standard deviation was found to be ± 2.1% for 50 mgL^{-1} of dye.

L. *Suggested Mechanism*

The transport mechanism of dyes can be explained as follows (Fig. 13):

- The extraction of anionic dyes from feed solution into hydrophobic membrane is accompanied by the presence of cationic TBAB carrier as ion pair complex [Dye$^+$ (TBA$^-$)].
- The resulting neutral ion paired complex is preferentially distributed into the organic membrane.
- The ion-pair thus formed diffuses across the membrane towards the membrane-strip solution interfaces as a result of concentration gradient.
- At the membrane-strip solution interface, the ion paired dye is released.
- This is confirmed by the presence of dye in the strip solution.

- The carrier diffuses back across the membrane to the feed solution-membrane interface, where the cycles starts again.

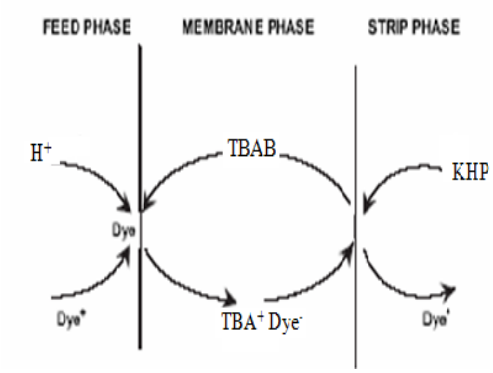


Fig. 13 Transport mechanisms of dyes

M. Application of the Developed SLM for Textile Wastewater

The developed SLM was tested for its applicability to real textile wastewater obtained from Chennai. The general characteristics of the textile wastewater are furnished in Table III, the pH of the textile effluent was adjusted to 7 ± 0.1 and the optimum conditions already obtained on LM were used to find out the percentage recovery of dyes. Under optimized condition the permeability coefficient was 8.60×10^{-4} mg/cm^2.s and 6.58×10^{-4} mg/cm^2.s for LBR E4BA and LBR E6BA. The recovery efficiencies are almost same for synthetic solution and textile effluent.

TABLE III GENERAL CHARACTERISTICS OF TEXTILE EFFLUENT*

S.no.	Parameters	Alkali Bath	Wash Bath
1	pH	9.8	9.3
2	Conductivity (mScm^{-1})	18.1	8.3
3	Nature of dye	Anionic	Anionic
4	Chloride (mgL^{-1})	120	95.5
5	Carbonate (mgL^{-1})	7,000	3,500
6	Bicarbonate (mgL^{-1})	650	75.4
7	Sulphate (mgL^{-1})	3000	250
8	Dye concentration (mgL^{-1})	50	15
9	COD (mgL^{-1})	900	450
10	TOC (mgL^{-1})	500	255
11	TDS (mgL^{-1})	10,500	4,700

* COD= chemical oxygen demand; TOC = total organic carbon; TDS= total dissolved solids

IV. CONCLUSION

The transport of dyes by TBAB-coconut oil SLM is studied and found that dyes can be very well recovered from aqueous solution at pH 7 ± 0.1 at 27^{0}C. It is noticed that the flux when increases with the increase in carrier concentration and permeability coefficient decreases with increase in initial dye concentration in feed phase. When membrane is used for a long time without reimpregnation, accumulation of dye was noticed. The maximum stripping efficiency was found in the range of 6.211×10^{-4} KHP solution. If this technique is introduced in wastewater treatment system the valuable constituent can be recovered most effectively and economically.

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